New Syntheses of *C*-Mercuriated Sugars and Rapid Conversion into Bromo-sugars by Reaction with Bromine Chloride from Sodium Bromide and Chloramine-T

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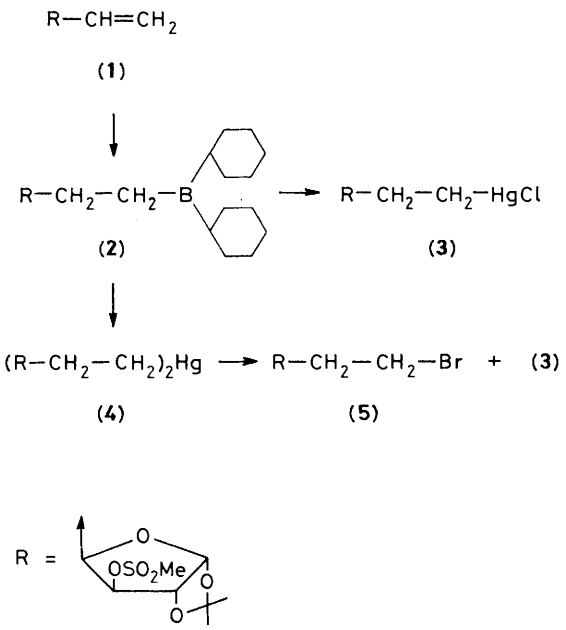
New *C*-mercuriated sugars have been synthesised *via* hydroboration–transmetallation sequences; the bis(glycosyl)mercury compound (**4**) reacts very rapidly with bromine chloride generated *in situ* from sodium bromide and chloramine-T, to give a high isolated yield of bromo-sugar (**5**) (87%).

Prompted by recent interest in the development of very rapid methods for the synthesis of complex organic molecules radiolabelled by halogens,[1] we have been interested in extending our earlier studies of derivatives which have a boron atom linked *via* a carbon of a sugar,[2] to other organometallic derivatives of carbohydrates. It has long been known that carbon–mercury bonds are cleaved rapidly by halogens[3] (I_2, Br_2, and Cl_2) and the products of the methoxy-mercuration of tri-*O*-acetyl-D-glucal have already been studied in this regard.[4] We now report new synthetic routes to *C*-mercuriated sugars and a method for rapid conversion into bromo-sugars.

Ten years ago, Brown and co-workers reported that mixed organoboranes (**2**), obtained by hydroboration of terminal olefins with dicyclohexylborane, readily react with one equiv. of mercury diacetate to yield primary alkyl-chloromercury derivatives, after reaction with sodium chloride.[5] With 0.5 equiv. of mercury diacetate, such organoboranes (**2**) yield bis-(primary alkyl)-mercury derivatives.[6] The application of both



these synthetic procedures to an unsaturated carbohydrate model (**1**) has permitted us to isolate the *C*-chloromercuriated sugar (**3**)† (m.p. 174—175 °C) in 78% yield and the bis-(glycosyl)mercury compound (**4**)† {m.p. 69—72 °C, $[\alpha]_D^{22}$ = −34.49° (*c* 0.8, $CHCl_3$)} in 71% yield. It is interesting to note that very recently, bis(glycosyl)mercury compounds were obtained by methoxy-mercuriation of enolic sugar derivatives.[7]

Conversion of alkenes into bromoalkanes *via* a hydroboration–transmetallation–bromination 'one pot' sequence has been reported,[8] using Br_2 as the brominating reagent. However, for incorporation of radiolabelling (starting with labelled bromide), the method of *in situ* generation of bromine chloride, used by Kabalka and co-workers to cleave the carbon–boron bond,[9] and by ourselves in our earlier studies,[2] is more appropriate. For this reason, we have studied the reaction of one equiv. of bromine chloride generated *in situ* with the bis-(glycosyl)mercury derivative (**4**); 1 mmol of NaBr in H_2O (2 ml) was added to a solution of 1 mmol of (**4**) in tetrahydrofuran (THF, 5 ml). The reaction mixture was cooled to 0 °C and shielded from light. Chloramine-T [2 mmol in 3 ml of a mixture of THF and water (1:1)] was added in one portion and then 3 ml of an aqueous 10% HCl solution, which had been saturated with NaCl, was added to the mixture. After 3 min the starting material was completely consumed to yield a precipitate which was filtered, washed with ether (2 × 15 ml), and identified as pure (**3**) (76%). The organic layer of the combined filtrates was separated, washed with water (2 × 10 ml), dried ($MgSO_4$), and concentrated. Column chromatography of the residue on silica yielded pure (**5**)† (87%) {m.p. 74—75 °C, $[\alpha]_D^{22}$ = + 6.50° (c 1, $CHCl_3$)}.

Considering the extremely mild reaction conditions, the very short reaction time, the known ease of generating [^{75}Br]-bromide (half-life 97 min), and the high isolated yield, this method appears to be ideally suited for the synthesis of radiolabelled (bromine) complex organic molecules for use with positron emission tomography.

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† All compounds had elemental microanalyses (C,H,Br) and ^{1}H n.m.r. spectra (270 MHz) in complete accord with the assigned structures.

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